

Article

Adsorption of SO₂ Molecule on Pristine, N, Ga-Doped and -Ga-N- co-Doped Graphene: A DFT Study

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Abstract: SO₂ (sulfur dioxide) is a toxic substance emitted into the environment due to burning sulfur-containing fossil fuels in cars, factories, power plants, and homes. This issue is of grave concern because of its negative effects on the environment and human health. Therefore, the search for a material capable of interacting to detect SO₂ and the research on developing effective materials for gas detection holds significant importance in the realm of environmental and health applications. It is well known that one of the effective methods for predicting the structure and electronic properties of systems capable of interacting with a molecule is a method based on quantum mechanical approaches. In this work, the DFT (Density Functional Theory) program DMol³ in Materials Studio was used to study the interactions between the SO₂ molecule and four systems. The adsorption energy, bond lengths, bond angle, charge transfer, and density of states of SO₂ molecule on pristine graphene, N-doped graphene, Ga-doped graphene, and -Ga-N- co-doped graphene were investigated using DFT calculations. The obtained data indicate that the bonding between the SO₂ molecule and pristine graphene is relatively weak, with a binding energy of −0.32 eV and a bond length of 3.06 Å, indicating physical adsorption. Next, the adsorption of the molecule on an N-doped graphene system was considered. The adsorption of SO₂ molecules on N-doped graphene is negligible; generally, the interaction of SO₂ molecules with this system does not significantly change the electronic properties. However, the adsorption energy of the gas molecule on Ga-doped graphene relative to pristine graphene increased significantly. The evidence of chemisorption is increased adsorption energy and decreased adsorption distance between SO₂ and Ga-doped graphene. In addition, our results show that introducing -Ga-N- co-dopants of an “ortho” configuration into pristine graphene significantly affects the adsorption between the gas molecule and graphene. Thus, this approach is significantly practical in the adsorption of SO₂ molecules.

Keywords: graphene; SO₂ adsorption; density functional theory; -Ga-N- co-doped graphene; gas sensor



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1. Introduction

Through contamination of the air by dangerous gas, SO₂ is a consequence of climate change, a significant factor in the climate system. This gas poses significant health risks to people. It is thought that toxic gas can cause adverse health effects, such as damage to living tissues and the central nervous system, severe illness, or, in extreme cases, death when ingested, inhaled, or absorbed by the skin or eyes [1,2]. The development of efficient SO₂ detection materials can facilitate the monitoring and mitigation of these environmental impacts.

Sensors are fast becoming a key instrument in solving these issues. The actual history of gas sensor development is more complex and multifaceted. The contributions of various scientists, engineers, and researchers have collectively shaped the field of gas

sensors. Nevertheless, one of the most critical events in 1962 was first studied by Seiyama T. and Taguchi N. using metal oxides (SnO_2) in semiconductor gas sensors [3]. After that, several scientists worldwide have begun to examine the development of new gas sensors, including those using silicon semiconductors and solid electrolytes. Various kinds of sensor materials, including MOS (metal oxide semiconductors), sulfides, binary lead chalcogenide nanomaterials, MOFs (metal-organic frameworks), van der Waals heterostructures, noble metals-based composites, have also been intensively published on other papers with their own advantages and disadvantages [4–9].

However, with the discovery of graphene in 2004 and the Nobel Prize winner for the development of graphene in 2010, graphene has become the object of attention in the world of science and innovation. Thus, the research community of gas sensors shifted their focus to a gas sensor based on graphene. Due to its two-dimensional nature and maximum surface-to-volume ratio, graphene is highly suitable for gas sensors based on surface interactions. Its low noise and high mobility lead to a high signal-to-noise ratio (SNR), critical for the sensor's detection limit. In addition, 2D materials can screen charge fluctuations better than 1D materials like carbon nanotubes (CNT). Nevertheless, it should be noticed that graphene-based gas sensors have some limits due to their zero-band gap property [10]. Moreover, pristine graphene has restrained adsorption capability for molecules [11] since it is inert. Also, no functional groups on the surface can interact with other molecules. A reasonable approach to tackle this issue could be modifying graphene by doping, which is still an active research area.

Doping graphene with other atoms or molecules is an efficient way to modify graphene's structural and electronic properties [12]. N-doped graphene is a modified form of graphene by replacing the carbon atoms in the supercell structure with a nitrogen atom. To realize the potential of graphene for electronics, a significant band gap should open in graphene. So far, various approaches, such as the application of an external electric field [13], chemical functionalization [14], and doping by impurities [15], have been proposed for opening a band gap in graphene. Among these, substitutional doping is proposed as the most effective method to modify the electrical properties of graphene. Nitrogen atom has received significant research attention as it is the nearest neighbor to carbon, which offers a high probability of entering the graphene lattice. There have been many reports on graphene band gap engineering using substitution doping [16].

Moreover, it has been observed that dopant metals on the graphene surface play an essential role in their use in gas-sensing applications [17]. Choosing gallium as a potential dopant metal for doping graphene over other elements such as gold and silver, the advantage, as noted by [18], is its weak chemical interaction with graphene, which preserves the integrity of the graphene lattice. Gallium is used to modify graphene because it can dissolve into graphene, and its small size and high mobility make it an effective dopant. Another advantage of gallium is that it is relatively easier to work with than to other dopants. It has a low melting point and evaporates quickly. Sharma S. and co-workers [19] suggest that gallium can effectively dope graphene and improve the reactivity and sensitivity of graphene to detect H_2S gas.

The Density Functional Theory (DFT) is one of the most popular and successful quantum mechanical approaches to matter. Today, it is commonly used to calculate, for example, the binding energies of molecules in chemistry and the band structure of solids in physics [20] to investigate the properties of solids in materials science. Moreover, researchers can calculate molecular geometries, rates and equilibria, spectra, and other physical properties with the density functional methods of computational chemistry [21]. The DFT method was the central theme of M. Khosravi [22] and her colleagues' study, in which the authors emphasized advantages such as simple formalism of the results, reduced computational costs, and improved accuracy. Also, X. Liang and his group [23], via DFT modeling, studied the adsorption of H_2O , NH_3 , CO , NO_2 , and NO on pristine and Ga-doped graphene. According to the results of the DFT calculation, a potential application of Ga-doped graphene for the detection of NO_2 gas was revealed. In addition,

the DFT method is widely used in many fields such as batteries [24], catalysis [25,26], drug modeling [27], photovoltaic devices [28], etc.

A high number of researchers have studied the effects of foreign element doping on the adsorption of graphene, in which they aimed to discover which doped system could enhance the sensitivity of graphene on gas molecules. An example is the study by Z. Zheng and co-workers [29], who investigated the adsorption properties of CO₂ gas molecules on X (B, N, P, Al)-doped mono-vacancy graphene. S. Rad and his team [30] used DFT calculations to evaluate the changes in the electrical properties of pristine and Al-doped graphene due to the adsorption of CO, CO₂, and H₂O molecules. There is a work by the authors Jiang M. and co-authors [31], where they studied the electronic and optical properties of graphene doped with gallium and nitrogen atoms. T. Xie and co-workers have performed density functional methods to investigate the adsorption of gases, including C₂H₂, CO, NO₂, and SO₂, on Co/N₃ co-doped graphene [32]. In [33], first-principles calculations were employed to investigate the adsorption structures, electronic characteristics, and gas-sensing properties of the pristine and B-, N-, P-, Al-, and Si-doped penta-graphene (PG) toward the NH₃, H₂S, and SO₂ molecules by G. Chen and co-workers.

Although extensive research has been carried out on graphene co-doped by -Ga-N-, no published work used graphene co-doped by -Ga-N- to reveal sensitivity to SO₂ molecules. As such, this study aimed to investigate the electronic properties of the graphene, N-doped graphene, Ga-doped graphene, and graphene co-doped by -Ga-N- on the interaction with SO₂ molecule by a first-principles simulation. These calculations were analyzed based on the density of states, electron density, and population analysis. We hope that our study provides valuable information for detecting toxic gas.

2. Computational Method

All the calculations were performed using density functional theory (DFT), implemented in the Dmol³ code [34] module in Materials Studio. We selected the widely used GGA-PBE functional to describe the interaction of electrons [35]. Convergence tolerances for geometry optimization were performed under quality to ensure good accuracy, which were set to Customized, 2×10^{-6} Ha energy, 0.004 Ha/Å maximum force, and 0.005 Å maximum displacement. The Grimme personalized method for DFT-D was utilized, which better describes Van der Waals functionalization [36]. The spin unrestricted setting was taken to use different orbitals for different spins. This study assessed the effect of using a double-sized numerical basis set plus p-functional (DNP). We used a basic (3.5) version of the basis files for our calculations. The smearing technique was applied to the occupied orbitals with a smearing value of 0.005 Ha (1 Ha = 27.2114 eV). A $10 \times 10 \times 1$ Monkhorst-Pack grid was set for the k-point meshes of Brillouin zone sampling in this study. The self-consistent (SCF) field tolerance was set as 1×10^{-6} Ha. The direct inversion of iterative subspace (DIIS) was used to accelerate the convergence of SCF charge density, and the DIIS size was set to 6 for further calculations. We constructed a $5 \times 5 \times 1$ non-edge hydrogenated supercell containing 50 C atoms with a vacuum space of 25 Å to prevent artificial interactions between the layers of the periodic system.

The electronic properties of the adsorption systems were analyzed based on the density of states, band structure, electron density, and population analysis. After that, we explored the adsorption energy of toxic molecules on the graphene layer according to the following Equation (1). Also, this is the basic adsorption energy formula for the rest of the systems, such as N-doped graphene, Ga-doped graphene, and -Ga-N- co-doped graphene.

$$E_{ads} = E_{graphene+gas} - E_{graphene} - E_{gas}, \quad (1)$$

herein, $E_{graphene+gas}$ is the total energy of graphene with adsorbed molecule, $E_{graphene}$ is the total energy of graphene, E_{gas} is the total energy of the molecule [37]. A negative E_{ads} (eV) value indicates stable adsorption. The more negative the E_{ads} value, the more stable the adsorbed structures. All the energy values are obtained based on the corresponding optimized geometries. The values of charge distribution and transfer were calculated by

the Mulliken charge analysis method [38]. The Mulliken charges on atoms were obtained from population analyses available in the Dmol³ module of Materials Studio.

3. Results and Discussion

3.1. Properties of the Structure

We start first calculating with the geometric structure of SO₂ was optimized to their steadiest configuration before studying their adsorption. Figure 1 displays the structure, and the information on bond lengths and angles is shown in Table 1.

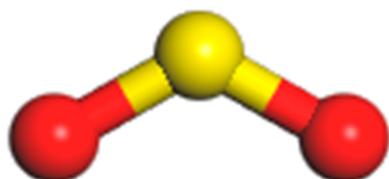


Figure 1. The structure of SO₂ molecule.

Table 1. Structural parameters of structure.

| Gas Molecule | Bond | Length (Å) | Angle (°) |
|-----------------|------|------------|-----------|
| SO ₂ | S-O | 1.47 | 119.9 |

3.2. Geometry of Pristine Graphene and Doped Graphene

Our calculation continued with creating a supercell of graphene according to the parameters of geometry optimization described in the computational method, where the C–C bond length calculated after optimization was found to be 1.42 Å, which agrees well with previous reports [39].

Upon doping graphene with a nitrogen atom, the structure of doped graphene changes significantly from a geometric point of view, as shown in Figure 2. Figure 2 displays pristine graphene's and N-doped graphene's geometric structure after relaxation. The N-doped graphene model was obtained by replacing one of the central carbon atoms with a nitrogen atom. For N-doped graphene, the C–N atom distance was found to be 1.41 Å. In this case, the concentration of the doped nitrogen in graphene had a 2% atomic ratio.

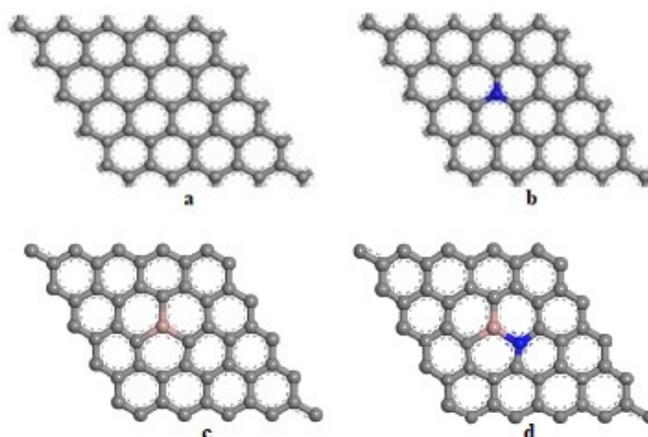


Figure 2. Relaxed geometries of 5 × 5 supercell of pristine graphene (a), where the carbon atoms are shown in grey and nitrogen-doped graphene (b), where the nitrogen atom is shown in blue; gallium-doped graphene (c), where the gallium atom is shown in pink; graphene co-doped by gallium and nitrogen atoms (d).

3.3. Adsorption of SO₂ on Pristine Graphene

After that, we investigated the configuration of the SO₂ molecule adsorbed on pristine graphene. We presented the adsorption models of the molecule on pristine graphene after optimization (Figure 3). The corresponding geometrical parameters, the adsorption parameters, and the charge transfer of the graphene + gas system are listed in Table 2.

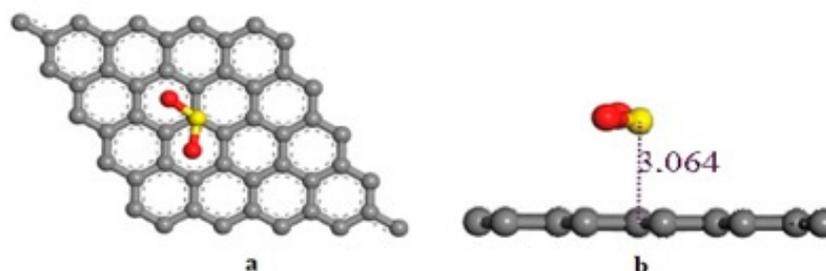


Figure 3. The top view (a) and side view (b) of graphene + SO₂ system.

Table 2. The detailed parameters of graphene + gas system.

| System | Adsorption Distance (Å) | Bond Length (Å) | Bond Angle (°) | E_{ads} (eV) | Q_T (e) |
|----------------------------|-------------------------|--|----------------|----------------|-----------|
| Graphene + SO ₂ | 3.06 | 1.48 (S-O ₁) 1.48 (S-O ₂) | 119.2 | −0.32 | −0.095 |

When comparing Tables 1 and 2, it is clearly seen that the geometrical parameters have changed. Table 2 summarizes the adsorption distance on the SO₂ molecule on pristine graphene, calculated bond length and bond angle of the molecule, adsorption energies, and charge transfer. As shown in Table 2, the adsorption of the SO₂ molecule on pristine graphene is weak due to its poor interactions between π electrons of graphene and the SO₂ molecule. The adsorption energy is only −0.32 eV for SO₂ on pristine graphene. The transfer charges between the SO₂ molecule and pristine graphene were −0.095 e. The negative charge transfer illustrated the charge transfer from pristine graphene to the SO₂ molecule. The low energy adsorption, low transfer charge, and far distance have indicated that pristine graphene has a weaker adsorption of the SO₂ molecule. Therefore, pristine graphene is not appropriate for the detection of SO₂ molecules. It is believed that the SO₂ molecule is physisorbed on pristine graphene. This could limit the sensitivity of pristine graphene for detecting SO₂ molecules.

3.4. Adsorption of SO₂ on N-Doped Graphene

The adsorptions of SO₂ molecules on N-doped graphene were studied, and the corresponding atomic structure is shown in Figure 4. The adsorption of SO₂ molecules on N-doped graphene is weak, so the interaction was not affected by the doped nitrogen atom. As listed in Table 3, the value is close to that between the pristine graphene and each SO₂ molecule, similar to the literature results [40]. These results indicate that the doped gallium atom could significantly improve the interaction between the nitrogen graphene and the SO₂ molecule.

3.5. Adsorption of SO₂ on Ga-Doped Graphene

Figure 5 depicts the optimized model of the structure of Ga-doped graphene. In this model, the bond length of the Ga-C bond is longer than the C-C bond length in the pristine graphene, where a bond length value of 1.86 Å is present because of the larger atomic radius of the Ga atom. This value is in good agreement with the previous report [23].

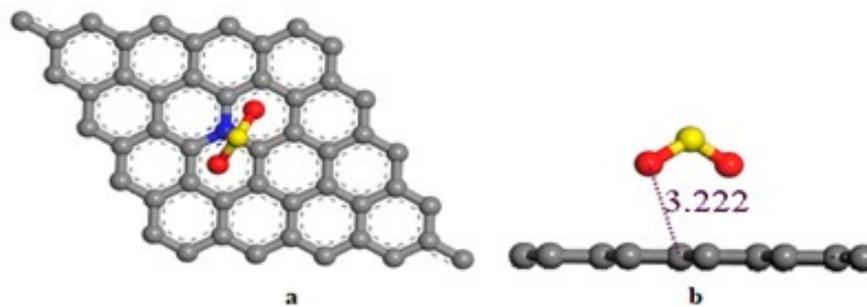


Figure 4. The top view (a) and side view (b) of nitrogen-doped graphene + SO₂ system.

Table 3. The detailed parameters of N-doped graphene+ gas system.

| System | Adsorption Distance (Å) | Bond Length (Å) | Bond Angle (°) | E _{ads} (eV) | Q _T (e) |
|------------------------------------|-------------------------|--|----------------|-----------------------|--------------------|
| N-doped graphene + SO ₂ | 3.22 | 1.51 (S-O ₁) 1.51 (S-O ₂) | 117.6 | −0.48 | −0.236 |

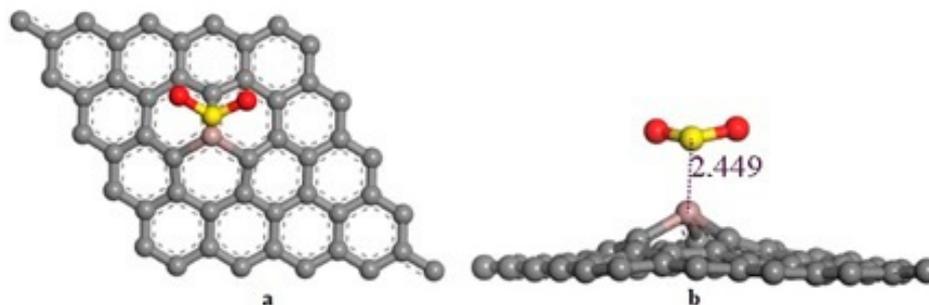


Figure 5. The top view (a) and side view (b) of gallium-doped graphene + SO₂ system.

To compare Tables 3 and 4, we found that adsorption energy is significantly increased after doping graphene with gallium. In addition, it is evident that the adsorption distance between the SO₂ molecule and Ga-doped graphene dramatically decreased. Consequently, the larger adsorption energy and shorter adsorption distance between the SO₂ molecule and Ga-doped graphene suggested that chemisorption had formed. As for the effect of co-doped N and metal atoms, it needs further discussion.

Table 4. The detailed parameters of the Ga-doped graphene + gas system.

| System | Adsorption Distance (Å) | Bond Length (Å) | Bond Angle (°) | E _{ads} (eV) | Q _T (e) |
|-------------------------------------|-------------------------|--|----------------|-----------------------|--------------------|
| Ga-doped graphene + SO ₂ | 2.45 | 1.49 (S-O ₁) 1.49 (S-O ₂) | 121.3 | −2.61 | −0.148 |

3.6. Adsorption of SO₂ on -Ga-N- co-Doped Graphene

Also, Figure 6 presents the structure optimization model of the -Ga-N- co-doped graphene. In this work, the adsorption sites of the toxic molecule were considered in order to find the position that exhibits the highest adsorption energy. All adsorption sites on -Ga-N- co-doped graphene were considered as follows: the bond-bridge (B-site), the center of hollow (H-site), and the center of the top (T-site) [11].

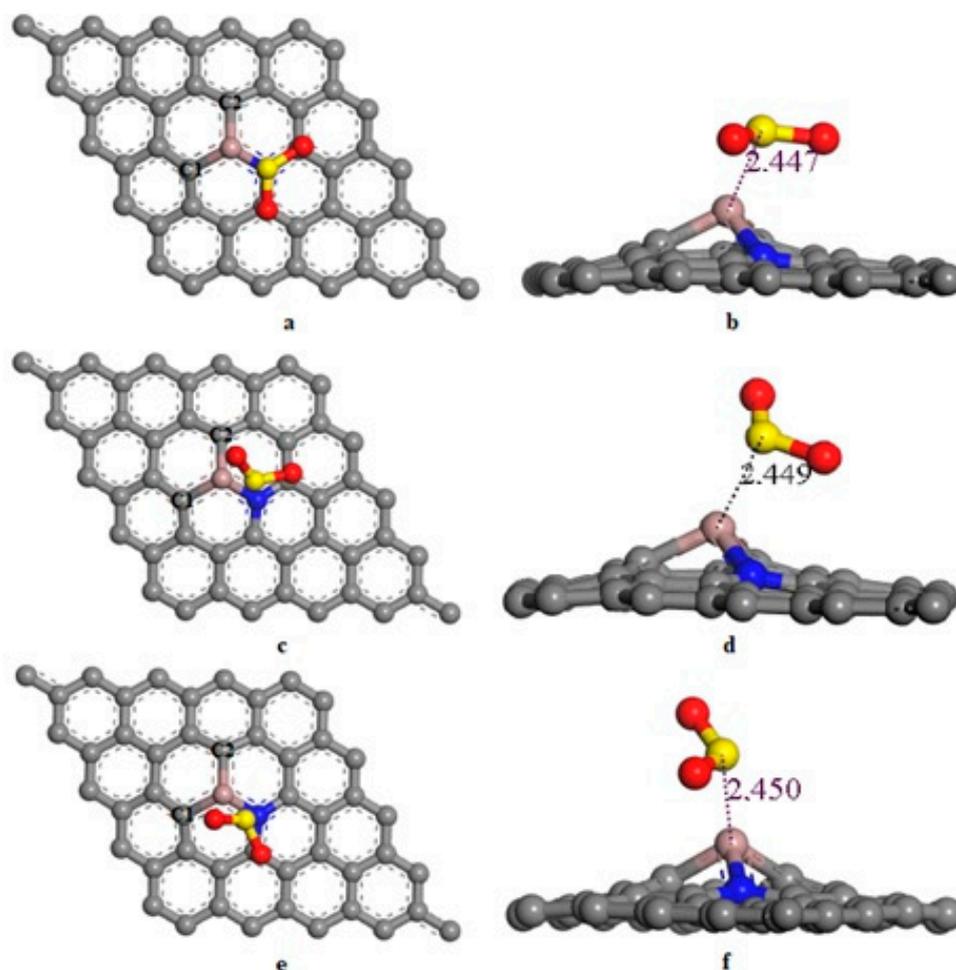


Figure 6. The top view (a) and side view (b) of -Ga-N- co-doped graphene + SO₂ system in the B site; the top view (c) and side view (d) of -Ga-N- co-doped graphene + SO₂ system in the H site; the top view (e) and side view (f) of -Ga-N- co-doped graphene + SO₂ system in the T site.

Before optimization, the bond length between gallium and nitrogen atoms was 1.71 Å. Meanwhile, due to the co-doping of the Ga and N atoms, the stress of the two C atoms around it in the system changed, causing them to move away from their original positions:

B site: C₁-Ga = 1.862 Å, C₂-Ga = 1.863 Å. We found that the bond length of Ga-N was 1.903 Å, while the angles of C₁-Ga-C₂, C₂-Ga-N, and C₁-Ga-N were 99.6°, 95.3° and 95.5°, respectively.

H-site: C₁-Ga = 1.861 Å, C₂-Ga = 1.863 Å. We observed that the bond length of Ga-N was 1.898 Å, while the angles of C₁-Ga-C₂, C₂-Ga-N, and C₁-Ga-N were 99.6°, 95.5° and 96.3°, respectively.

T-site: C₁-Ga = 1.864 Å, C₂-Ga = 1.863 Å. In this position, we found that the bond length of Ga-N was 1.901 Å, while the angles of C₁-Ga-C₂, C₂-Ga-N, and C₁-Ga-N were 99.3°, 95.8° and 95.3°, respectively. As shown in Table 5, we found that all initial B, H, and T configurations were almost changed. After optimization, the configurations did not keep their original adsorption site. The results of the adsorption energy indicate that the absorption on the H site is the most stable configuration, and the stability order is H < T > B.

Table 5. The detailed parameters of the -Ga-N- co-doped graphene + gas system.

| System | Adsorption Site | Adsorption Distance (Å) | Bond Types (Å) | Bond Length (Å) | Bond Angle (°) | E_{ads} (eV) | Q_T (e) |
|--|-----------------|-------------------------|----------------|--|----------------|----------------|-----------|
| -Ga-N- co-doped graphene + SO ₂ | B | 2.447 | 1.903 (Ga-N) | 1.507 (S-O ₁) 1.507 (S-O ₂) | 120.8 | -2.75 | -0.258 |
| | H | 2.449 | 1.898 (Ga-N) | 1.504 (S-O ₁) 1.497 (S-O ₂) | 120.6 | -2.55 | -0.214 |
| | T | 2.450 | 1.901 (Ga-N) | 1.504 (S-O ₁) 1.498 (S-O ₂) | 120.5 | -2.53 | -0.218 |

For a better understanding of the electronic properties of the presented systems before and after interaction with SO₂ molecules, it is necessary to analyze their DOS. According to the above analysis of adsorption parameters, the most easily adsorbed configurations are chosen on the corresponding surfaces of graphene structures.

Firstly, consider the DOS before and after the adsorption of the SO₂ molecule by the pristine graphene, shown in Figure 7a. As can be seen, the DOS of graphene agrees with the literature results and reflects well with its electronic properties. After the adsorption of the SO₂ molecule, the DOS increases at -21 eV, -11 eV, -7 eV, -3.5 eV, and 1 eV above the Fermi level, which causes an increase in the total density of states. However, the DOS at the Fermi level is almost unchanged, indicating that the conductivity change is not apparent after the adsorption of SO₂ by the pristine graphene. Also, the results of all the above discussions showed that the pristine graphene is not sensitive to the SO₂ molecule, and only weak physical adsorption is detected. Thus, graphene is not suitable for the detection of SO₂ molecules.

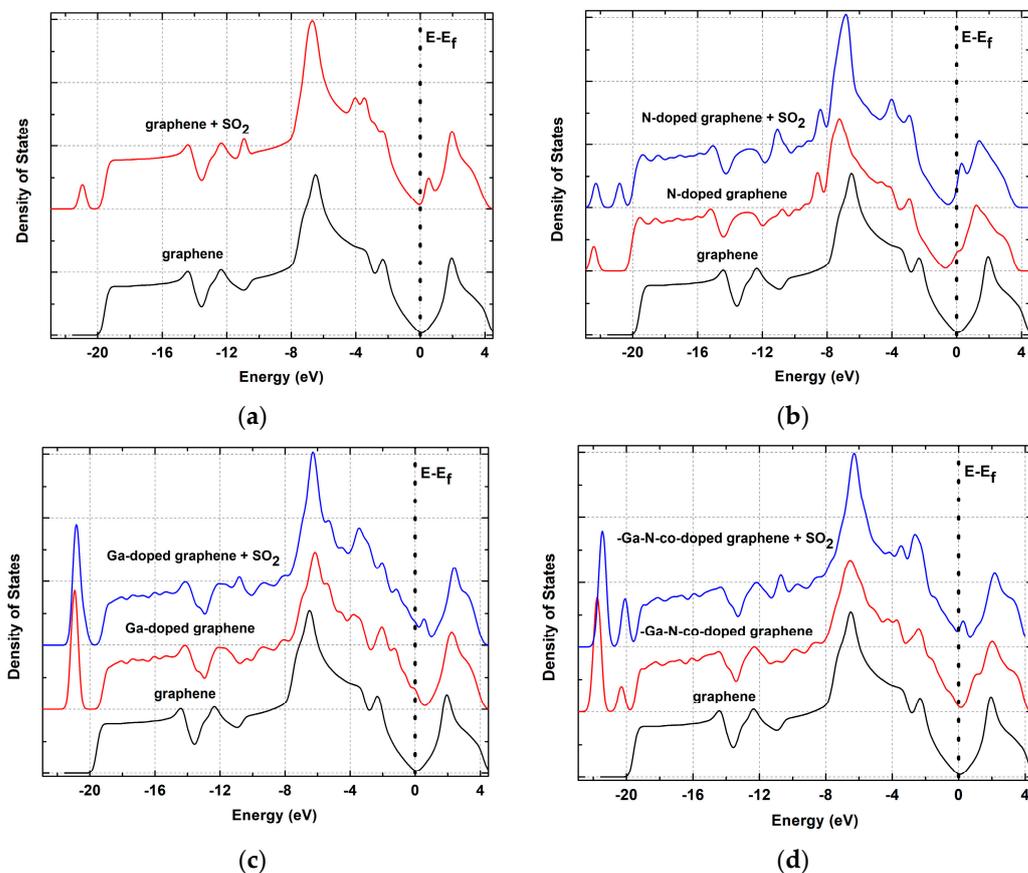


Figure 7. DOS of SO₂ molecule adsorption on pristine graphene (a), N-doped graphene (b), Ga-doped graphene (c) and -Ga-N- co-doped graphene (d).

The DOS of N-doped graphene, according to the type of substitution of carbon atom by nitrogen, is shown in Figure 7b. As can be seen from the DOS, nitrogen doping of graphene leads to its changes; there is an increase in density at -23 eV, -8.5 eV, and at the Fermi level. This is reflected in the overall density of states. It should also be noted that nitrogen doping of graphene leads to a downward shift of the Dirac point of graphene and the Fermi level towards the conduction band. This indicates that the conduction type of N-doped graphene becomes electronic (n-type). Adsorption of the SO_2 molecule on N-doped graphene leads to additional changes in DOS in the form of an increase in the density of states at -21 eV, -11 eV, and -4.1 eV, while no significant changes are observed at the Fermi level. The results of DOS calculation of the Ga-doped graphene system by substitution type followed by adsorption of SO_2 molecule are shown in Figure 7c. As can be seen from the DOS, the doping of graphene with gallium leads to significant changes at the density of states -21 eV, -11 eV, and in the range from -6 to -0.5 eV, the appearance of states is observed. In the adsorption of the SO_2 molecule, an additional shift of the Fermi level towards the valence band with a slight change in the density of states at the Fermi level is observed. The DOS structure of -Ga-N-co-doped graphene in the “ortho” configuration is shown in Figure 7d, where it is observed that the density of states changes markedly at -21.8 , -20.5 , -9.5 , -8.5 , -3.9 , -1.7 , and -0.5 eV. As a result of the interaction of this system with the SO_2 molecule, there is a shift of the Fermi level towards the valence band, and at the same time, there is an increase in the density of states at the Fermi level. This fact indicates the existence of orbital hybridization in the adsorption system, and this confirms that there is chemisorption of SO_2 molecule on -Ga-N- co-doped graphene. In this case, a change in the electrical properties of this system is expected.

4. Summary and Conclusions

In conclusion, the electronic properties of pristine graphene, N-doped graphene, Ga-doped graphene, and -Ga-N- co-doped graphene are investigated based on the DFT calculations. This study aimed to determine how effectively doping graphene with N, Ga and -Ga-N- co-doped graphene affects the sensitivity of the SO_2 molecule. The data obtained from DFT calculations confirm the well-known inert properties of pristine graphene, i.e., the nature of the interaction is physisorbed. No significant differences in adsorption energy were found between N-doped graphene and SO_2 molecules. On the contrary, the adsorption of SO_2 on Ga-doped graphene is chemisorption. The addition of gallium and nitrogen atoms drastically changes the electronic structure of graphene and may be a good candidate for sensing this toxic gas SO_2 . These results imply that -Ga-N- co-doped graphene shows the most incredible ability to interact with SO_2 and is a promising gas detection system for future sensors.

Author Contributions: Conceptualization, D.A., A.I. and G.B; methodology, N.G; software, D.A. and N.G; validation, D.A., A.I. and N.G.; formal analysis, G.B.; investigation, D.A., A.I. and N.G.; resources, D.A. and N.G; data curation, D.A. and N.G; writing—original draft preparation, D.A.; writing—review and editing, D.A. and A.I.; visualization, D.A.; supervision, D.A. and A.I.; project administration, D.A. All authors have read and agreed to the published version of the manuscript.

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